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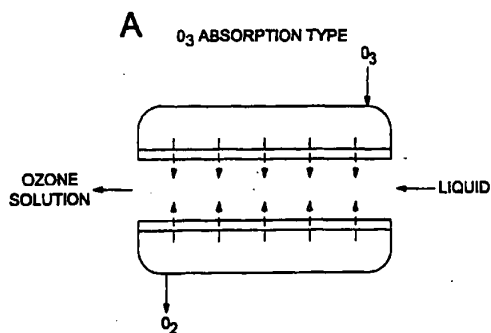
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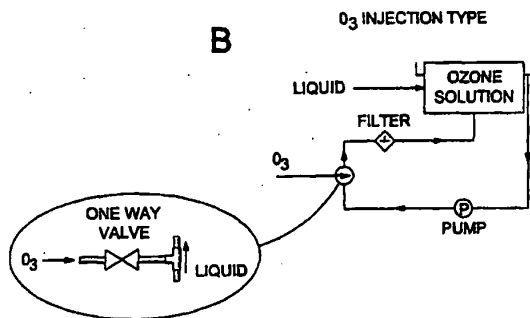
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AN ACIDIC OZONE SOLUTION HAVING A HIGH OZONE CONTENT, A METHOD FOR PREPARING THE SOLUTION, AND A CLEANING METHOD USING THE SOLUTION



(57) Abstract: The present invention relates to an acidic ozone solution having a high concentration of ozone, a method for preparing the solution by injecting ozone into an acid, and a method for cleaning single crystal silicon wafers using the solution.



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**AN ACIDIC OZONE SOLUTION HAVING A HIGH OZONE CONTENT,  
A METHOD FOR PREPARING THE SOLUTION,  
AND A CLEANING METHOD USING THE SOLUTION**

The present invention relates generally to an ozone  
5 solution having a high concentration of ozone, a method for  
preparing the solution, and a method for cleaning single  
crystal silicon wafers using the solution.

The continuing reduction in the device geometry of  
integrated circuits has resulted in increasing sensitivity  
10 to surface contaminants such as transition metals and  
organic compounds both on the surface of semiconductor  
wafers used for device manufacturing and at numerous steps  
throughout the device manufacturing process. For example,  
transition metals either existing on the initial wafer  
15 surface or deposited during device manufacturing can  
adversely affect the electrical characteristics of an  
electronic device.

The manufacture of semiconductor wafers requires  
numerous processing operations such as slicing, lapping,  
20 etching, and polishing, generally resulting in a variety of  
contaminants on the surface of the wafer. Typical  
contaminants include transition metal impurities such as  
iron, copper, chromium, nickel, and similar metals such as  
alkaline metals, as well as various organic compounds.  
25 Furthermore, the surface of both the initial wafer and  
device layers formed thereon may be contaminated during the  
device manufacturing processes. Therefore, semiconductor  
wafer and device manufacturers typically subject the wafer  
to one or more cleaning processes during the manufacture of  
30 the wafer, after the manufacture of the wafer but before  
device manufacturing, and at numerous points throughout the  
device manufacturing process.

There are a variety of cleaning methods known in the  
art to reduce the concentration of surface contaminants  
35 (e.g., RCA cleaning, Piranha-RCA cleaning, megasonic and  
ultrasonic cleaning, scrubbing and acid etching.)  
Conventional cleaning methods generally use large quantities  
of highly concentrated solutions of acid, alkali or hydrogen

peroxide. Accordingly, the waste solutions produced by conventional cleaning methods must be properly treated prior to disposal which increases the production cost.

It is known that the surface of a semiconductor wafer or device may be cleaned by contacting the surface with an aqueous ozone solution (i.e., ozone or ozonated water) to remove both transition metals and organic contaminants. In fact, ozone water has a number of potential applications in the semiconductor industry, such as depositing oxide layers having reduced contaminants on the surface of silicon wafers or devices, or removing photoresist from the surface of a device during the device manufacturing process. However, in each of these applications, the effectiveness of ozonated water is limited by the low solubility of ozone in water (See, e.g., United States Patent No. 5,971,368.)

For example, in traditional cleaning processes wherein a wafer is submersed in an ultrapure water ozone solution, the maximum concentration of ozone is about 30 ppm at ordinary temperature in a once through cleaning process, and is not more than 50 ppm at ordinary temperature in a circulating cleaning tank. Such limited concentrations result in long cleaning times for removing transition metals and or organic compounds. In addition, ozone has a limited stability in solution and tends to effervesce out of solution such that the concentration decreases with time. Thus, ozone must typically be continuously added to the solution to maintain the desired concentration.

Several attempts have been made to increase the concentration of ozone in solution. For example, United States Patent No. 5,971,368 discloses a process wherein ozone is added to ultrapure water or other liquid in a pressurized vessel, to produce an ozone solution which is then sprayed on the surface of a wafer to oxidize the surface. In one example, the initial concentration of ozone in an ultrapure water ozone solution is 50 ppm. The ozone water must be maintained at high pressure to prevent the ozone from effervescing out of the solution.

United States Patent No. 5,464,480 discloses a process where a high concentration ozone water is said to be obtained by mixing ozone and water at a subambient temperature ranging from about 1 °C to about 15 °C. However, while the solubility of ozone in water does increase with decreasing temperature, the concentration of ozone in water even at a temperature as low as 1 °C is less than 40 ppm. Furthermore, to maintain the elevated ozone concentration, the solution must be maintained at the lower temperature, increasing the complexity of the semiconductor cleaning process equipment and increasing the cost of wafer cleaning processes.

In view of the foregoing, a need continues to exist for an ozone solution comprising a high concentration of ozone and a process for producing such a solution.

#### SUMMARY OF THE INVENTION

Among the objects of the present invention may be noted the provision of an aqueous solution comprising a high concentration of ozone; the provision of an acidic aqueous solution comprising ozone; the provision of a method for preparing the solution; the provision of a method for cleaning a single crystal silicon surface using the solution; and, the provision of a method for cleaning a single crystal silicon surface having a semiconductor device thereon using the solution.

Generally, the present invention is a method for preparing an acidic ozone solution comprising injecting gaseous ozone into a liquid acid selected from the group consisting of organic acids having fewer than 20 carbon atoms, hydrochloric acids and mixtures thereof. The solution may then be diluted with water. Alternatively, the liquid acid may be diluted prior to the injection of ozone.

The present invention is further directed to directed to an acidic ozone solution comprising ozone and an acid selected from the group consisting of organic acids having

fewer than 20 carbon atoms, hydrochloric acids and mixtures thereof, the acidic ozone solution having an ozone concentration of at least about 55 ppm.

The present invention is still further directed to a  
5 method for cleaning a surface of a semiconductor wafer  
comprising contacting the surface with an acidic ozone  
solution comprising ozone and an acid selected from the  
group consisting of organic acids having fewer than 20  
carbon atoms, hydrochloric acids and mixtures thereof, the  
10 acidic ozone solution having an ozone concentration of at  
least about 55 ppm.

Other objects and features will be in part apparent and  
in part pointed out hereinafter.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1(a) shows an absorption-type dissolution system  
for dissolving a gas in a liquid.

Figure 1(b) shows an injection-type dissolution system  
for dissolving a gas in a liquid.

#### DETAILED DESCRIPTION OF THE INVENTION

20 It has been discovered that the concentration of ozone  
in a liquid ozone solution can be increased if the solution  
further comprises an acid. Accordingly, an acidic ozone  
solution having an ozone concentration of 55 ppm or more is  
provided. Advantageously, the high concentration ozone  
25 solution can be used to clean silicon wafers.

The present invention uses as a starting material a  
particular acid selected from the group consisting of an  
organic acid having 20 carbon atoms or less, hydrochloric  
acid and mixtures thereof. When a mixture of organic acid

with hydrochloric acid is used, the precise ratio between the organic acid and hydrochloric acid is not critical to the present invention and may be varied without departing from the scope of the present invention.

- 5       Organic acids suitable for use in the present invention may be selected from carboxylic acids (e.g., lower and higher fatty acids), including monocarboxylic acids, dicarboxylic acids and tricarboxylic acids, whether saturated or unsaturated (including optical isomers
- 10 thereof), halogenated acids of said carboxylic acids, oxy-mono or dicarboxylic acids (including optical isomers), aromatic carboxylic acids, amino acids and other organic acids such as ascorbic acid, gluconic acid, alginic acid and glutathione. Specific examples of organic acids suitable
- 15 for use in the present invention include: formic acid, acetic acid, propionic acid, butyric acid, n-valeric acid, i-valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, caproic acid, citric acid, palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid, oxalic acid,
- 20 malonic acid, succinic acid, adipic acid, glutaconic acid, maleic acid, fumaric acid, lactic acid, citric acid, malic acid, tartaric acid, aspartic acid, glutamic acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, isophthalic acid, picolinic acid and protocatechuic acid.
- 25 These organic acids may be used singly or in combination of two or more. Preferably, an oxycarboxylic acid and more preferably citric acid is used. Furthermore, when preparing a solution to clean the surface of a silicon wafer, it is preferable to use a mixture of citric acid and hydrochloric
- 30 acid. Such a mixture is believed to be particularly effective at cleaning the surface of a silicon wafer. However, any of the above listed acids or mixtures thereof may be used to clean the surface of a wafer without departing from the scope of the invention.
- 35       The initial concentration of the acid prior to injecting the ozone is preferably at least about 0.005 percent by weight, more preferably at least about 0.01

percent by weight, still more preferably at least about 0.1 percent by weight, and may be as high as the maximum concentration of acid achievable based on the particular acid chosen. Initial acid concentrations less than 0.005 percent by weight typically do not allow concentrations of ozone in the final solution to be much greater than conventionally prepared ozone solutions and are therefore not preferred. Higher concentrations of acid allow for much higher ozone concentrations.

However, high concentrations of acid are typically not desirable for cleaning silicon wafers. For example, in a preferred wafer cleaning acidic ozone solution comprising citric acid and hydrochloric acid, the concentration of citric acid is preferably from about 0.1 percent by weight to about 1.0 percent by weight and the concentration of hydrochloric acid is from about 0.1 percent by weight to about 1.0 percent by weight. Accordingly, if the ozone solution is for use in cleaning a silicon wafer, the concentration of acid is preferably from about 0.005 percent by weight to about 5 percent by weight, and is more preferably from 0.05 percent by weight to about 5 percent by weight. However, higher acid concentrations may be used without departing from the scope of the present invention. Moreover, the concentration of acid may vary according to the particular acid chosen.

Typically, the ozone concentration in the gaseous ozone injected into the acid is from about 5 percent to about 20 percent by weight and is preferably about 10 percent to about 20 percent by weight. Gaseous ozone may be produced using a variety of known methods (e.g., surface electrode, double tube discharge or decomposition of distilled water). Ozone gas generators using such methods are commercially available. For example, an ozone gas generator which produces ozone gas by decomposing distilled water is commercially available from Permelec Electrode Ltd. The precise concentration and source of the gaseous ozone is not critical to the present invention however, variations in the

ozone concentration may effect the required rate and/or duration at which it must be blown into the acid solution to achieve the desired concentration of ozone in the acidic ozone solution.

5           Gaseous ozone is injected into the acid to produce an acidic ozone solution by directly blowing ozone into a liquid acid for a period of time. The precise manner in which ozone is blown into the liquid acid is not critical to the present invention and may be achieved using a variety of  
10   dissolution apparatuses. For example, the ozone may be blown into the liquid acid using an absorption-type dissolution apparatus as shown in Figure 1(a), or an injection type dissolution apparatus as shown in Figure 1(b). Dissolution apparatuses suitable for blowing ozone  
15   into liquid acid are commercially available, for example, model O-2147 dissolution apparatus available from S.E.S. Co., Ltd.

Typically, the liquid acid is at a gauge pressure of from about 50 kPa to about 100 kPa while injecting the  
20   gaseous ozone, although lower or higher pressures can be employed. The temperature of both the gaseous ozone and the liquid acid is typically from about 1 °C to about 60 °C and is preferably from about 1 °C to about 30 °C. The rate, duration and manner in which the ozone is blown into the  
25   acid should be sufficient to achieve the desired ozone concentration in a reasonable time. Preferably, the acidic ozone solution produced has an ozone concentration of at least about 55 ppm, more preferably at least about 60 ppm and still more preferably at least about 70 ppm. Typically,  
30   ozone is blown into the acid solution at a rate of from about 0.3 liter/minute to about 20 liter/minute, preferably from about 1 liter/minute to about 6 liter/minute for a period of time ranging from about 3 minutes to about 90 minutes, preferably from about 20 minutes to about 40  
35   minutes. The precise rate and duration of ozone injection depends on the desired ozone concentration, the acid used, and the injecting environment (i.e., the fluid



hydrodynamics, mass transfer rates, temperature, etc.). Accordingly, the rate and duration of ozone injection may vary considerably without departing from the scope of the present invention. As noted above, injecting ozone into acids of higher concentration allow for much higher ozone concentrations to be achieved. For example, ozone concentrations ranging from at least about 100 ppm to about 2000 ppm or greater are possible in highly concentrated acid solutions. The acidic ozone solution may then be diluted with water if necessary to reduce the concentration of acid and/or ozone to concentrations desired for use as a cleaning solution in semiconductor wafer and device manufacturing applications.

The desired acid concentration in the acidic ozone solution may be achieved by diluting the high concentration acid/ozone solution with ultrapure water (i.e., water suitable for use in semiconductor wafer and device manufacturing processes) after blowing ozone into the liquid acid. Alternatively, the desired acid concentration in the acidic ozone solution may be achieved by diluting the liquid acid with ultrapure water prior to injecting the ozone. That is to say, the acid itself or a diluted aqueous acid solution may be used as a solvent for the ozone.

Preferably, the ultrapure water has a purity profile suitable for use in semiconductor wafer and device manufacturing. As an example, semiconductor wafer and device manufacturing processes currently require the ultrapure water to contain less than 1 particle per ml having a diameter greater than  $0.05\ \mu\text{m}$ , less than 100 ppt of metallic contamination, less than 100 ppt of ionic contamination, less than 1 ppb organic contamination, less than 0.1 ppb of dissolved oxygen, less than 1 ppb silicon dioxide and less than 0.0001 cfu/ml of bacteria and has a resistivity of greater than 18 Ohm-cm.

The acidic ozone solution produced above may be used to clean a surface of a silicon wafer by contacting the surface of the wafer with the acidic ozone solution. The surface of

the wafer may be contacted with the acidic ozone solution by any means known in the art such as spraying the solution on the surface of the wafer. Preferably, however the surface of the wafer is contacted with the ozone solution by  
5 immersing the wafer in the solution. The wafer is maintained in contact with the acidic ozone solution for at least about 1 minute to about 30 minutes, preferably about 2 minutes to about 10 minutes. In general, the wafer may be contacted for longer periods of time without departing from  
10 the scope of the invention, however the purity of the wafer surface does not typically improve substantially. Upon contacting the surface of the wafer with the aqueous ozone solution, the acid concentration removes metal contaminants, and the ozone decomposes and removes organic contaminants  
15 thus improving the quality of the surface of the wafer.

The present invention is illustrated by the following example which is merely for the purpose of illustration and is not to be regarded as limiting the scope of the invention or manner in which it may be practiced.

20

EXAMPLE

As the following example illustrates, the present invention provides a method for the preparation of an acidic ozone solution containing a high concentration of ozone.

An acidic ozone solution having an ozone concentration  
25 of about 70 ppm was prepared by blowing gaseous ozone into a liquid acid at a gauge pressure of about 49 kPa to about 98 kPa at a rate of about 6 liters/min. The liquid acid was prepared by diluting citric acid with ultrapure water to produce a

liquid acid having a concentration of citric acid of about 0.01 percent by weight. The resulting solution was found to be effective at removing organic substances and metals from the surface of wafers.

- 5        In view of the above, it will be seen that the several objects of the invention are achieved. As various changes could be made in the above-described semiconductor substrate flattening process without departing from the scope of the invention, it is intended that all matters contained in the
- 10 above description be interpreted as illustrative and not in a limiting sense. In addition, when introducing elements of the present invention or the preferred embodiment(s) thereof, the articles "a," "an," "the" and "said" are intended to mean that there are one or more of the elements.
- 15 The terms "comprising," "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

**WHAT IS CLAIMED IS:**

1. A method for preparing an acidic ozone solution, the method comprising injecting gaseous ozone into a liquid acid selected from the group consisting of organic acids having fewer than 20 carbon atoms, hydrochloric acid and  
5 mixtures thereof to form the acidic ozone solution, the acidic ozone solution having a concentration of at least about 55 ppm ozone.
2. The method of claim 1 wherein the liquid acid is at a gauge pressure of from about 50 kPa to about 100 kPa while injecting the gaseous ozone.
3. The method of claim 1 wherein the concentration of ozone in the acidic ozone solution is at least about 60 ppm.
4. The method of claim 1 wherein the concentration of ozone in the acidic ozone solution is at least about 70 ppm.
5. The method of claim 1 wherein the concentration of acid in the liquid acid is at least about 0.005 percent by weight.
6. The method of claim 1 further comprising diluting the acidic ozone solution with water.
7. The method of claim 6 wherein the concentration of ozone in the acidic ozone solution prior to dilution with water is at least about 100 ppm.
8. The method of claim 1 wherein the liquid acid is diluted with water prior to injecting the gaseous ozone.

9. The method of claim 8 wherein the concentration of acid in the diluted liquid acid is at least about 0.005 percent by weight.

10. The method of claim 1 wherein the organic acid is selected from the group consisting of carboxylic acids, halogenated carboxylic acids, oxy-mono or dicarboxylic acids, aromatic carboxylic acids, amino acids, ascorbic acid, gluconic acid, alginic acid, glutathione and mixtures thereof.

11. The method of claim 1 wherein the organic acid is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, n-valeric acid, i-valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, caproic acid, citric acid, palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid, oxalic acid, malonic acid, succinic acid, adipic acid, glutaconic acid, maleic acid, fumaric acid, lactic acid, citric acid, malic acid, tartaric acid, aspartic acid, glutamic acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, isophthalic acid, picolinic acid, protocatechuic acid and mixtures thereof.

12. An acidic ozone solution comprising ozone and an acid selected from the group consisting of organic acids having 20 carbon atoms or less, hydrochloric acid and mixtures thereof, the acidic ozone solution having an ozone concentration of at least about 55 ppm.

13. The acidic ozone solution of claim 12 wherein the concentration of ozone is at least about 60 ppm.

14. The acidic ozone solution of claim 12 wherein the concentration of ozone is at least about 70 ppm.

15. The acidic ozone solution of claim 12 wherein the concentration of acid is at least about 0.005 percent by weight.

16. The acidic ozone solution of claim 12 wherein the concentration of acid is from about 0.005 percent by weight to about 5 percent by weight.

17. The acidic ozone solution of claim 12 wherein the organic acid is selected from the group consisting of carboxylic acids, halogenated carboxylic acids, oxy-mono or dicarboxylic acids, aromatic carboxylic acids, amino acids, ascorbic acid, gluconic acid, alginic acid, glutathione and mixtures thereof.

18. The method of claim 12 wherein the organic acid is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, n-valeric acid, i-valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, caproic acid, citric acid, palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid, oxalic acid, malonic acid, succinic acid, adipic acid, glutaconic acid, maleic acid, fumaric acid, lactic acid, citric acid, malic acid, tartaric acid, aspartic acid, glutamic acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, isophthalic acid, picolinic acid, protocatechuic acid and mixtures thereof.

19. A method for cleaning a surface of a semiconductor wafer comprising contacting the surface with an acidic ozone solution comprising ozone and an acid selected from the group consisting of organic acids having 20 carbon atoms or less, hydrochloric acid and mixtures thereof, the acidic ozone solution having an ozone concentration of at least about 55 ppm.

20. The method of claim 19 wherein the organic acid is selected from the group consisting of carboxylic acids, halogenated carboxylic acids, oxy-mono or dicarboxylic acids, aromatic carboxylic acids, amino acids, ascorbic acid, gluconic acid, alginic acid, glutathione and mixtures thereof.

21. The method of claim 19 wherein the organic acid is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, n-valeric acid, i-valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, caproic acid, citric acid, palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid, oxalic acid, malonic acid, succinic acid, adipic acid, glutaconic acid, maleic acid, fumaric acid, lactic acid, citric acid, malic acid, tartaric acid, aspartic acid, glutamic acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, isophthalic acid, picolinic acid, protocatechuic acid and mixtures thereof.

FIG. 1A

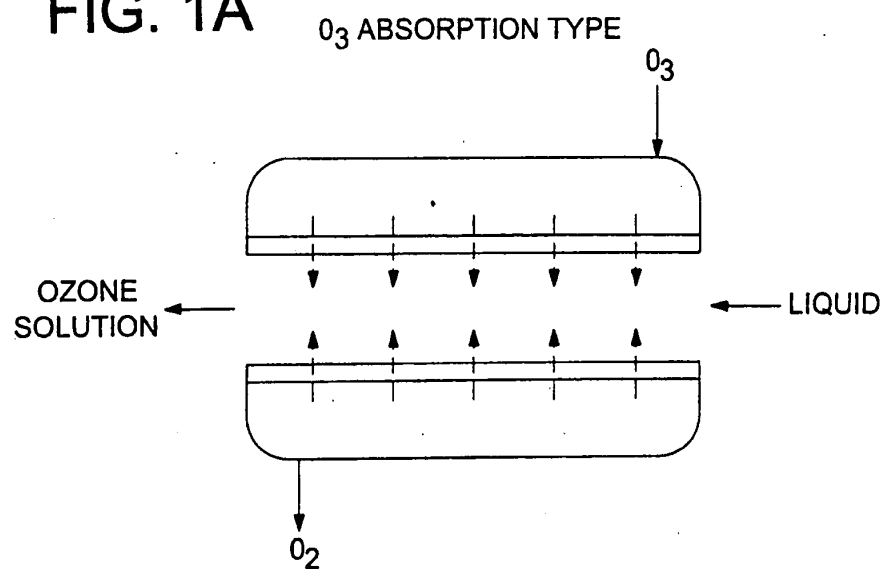
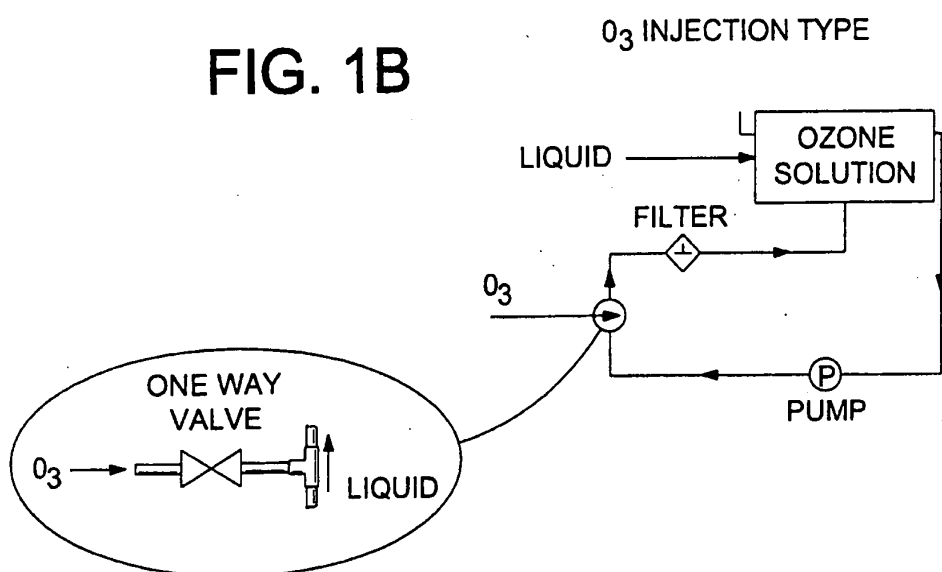


FIG. 1B





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19444

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C01B13/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*G\* document member of the same patent family

Date of the actual completion of the international search

27 October 2000

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08/11/2000

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19444

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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